



Comparative study of IVB–VIB transition metal compound electrocatalysts for the hydrogen evolution reaction

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ABSTRACT

A systematic and comparative investigation of 18 different IVB–VIB transition metal carbides, nitrides, sulfides, silicides and borides as well as of the three main group element ceramics AlN, B₄C and h-BN for their electrocatalytic performance towards the hydrogen evolution reaction (HER) is presented. We exploited the voltammetry of immobilised particles as a method that allows a rapid electrocatalyst screening and characterisation. The performances of the electrocatalysts – by means of the overpotential of the hydrogen evolution reaction in 100 mM H₂SO₄ – were compared with platinum and nickel as benchmarks. Although none of the catalyst materials investigated reached the performance of platinum with respect to overpotential and stability, the electrocatalytic properties of several compounds, i.e. tungsten and molybdenum carbide but also of tungsten boride calls for continuative work.

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1. Introduction

Hydrogen can be considered as a major chemical and energy currency of the future [1]. It can be readily converted for energy purposes (by combustion and in fuel cells) and it is vital as a reduction/hydration reactant for a great variety of chemical processes. Beside hydrogen storage and transport the sustainable generation of hydrogen – especially in the required quantities – represents a grand challenge [2]. Water electrolysis is a major path that aims at the use of electricity from renewable sources like wind and solar energy, for hydrogen production [3,4]. Fundamentally, this conversion process can also be considered as a possible solution to convert electrical energy during electricity excess into a storable, chemical form that in turn can be released upon electricity shortage [4]. So far, energy efficient low temperature electrolytic hydrogen evolution relies on the use of noble metals like platinum or palladium as electrocatalysts [5]. Yet, their high prices, growing demands and very limited resources are severe obstacles for world wide and large scale applications. Consequently, a wide range of non-noble electrocatalysts have been studied to overcome this bottleneck. Especially for alkaline electrolyzers a great variety of metal (e.g., nickel, nickel alloys) and metal oxide electrocatalysts have been proposed as replacement for platinum [6]. For acidic conditions, i.e. proton exchange membrane (PEM) electrolysis, however the

situation is less comfortable: most metal oxides and non-noble metals suffer from their instability at low pH values and thus the number of potential catalyst materials dwindles. For application under such conditions, the use of transition metal complexes has been proposed [7].

Group IVB–VIB transition metal carbides and nitrides, often referred to as interstitial alloys [8,9] (the carbon and nitrogen atoms occupy the interstitial lattice positions of the metal), possess properties known from the group VIII metals, like of the precious metals platinum or palladium [10]. They show remarkable catalytic activities, which have been attributed to their distinct electronic structure, induced by the presence of carbon, nitrogen or of phosphorus in the metal lattice [11]. In the case of tungsten carbide (WC and W₂C), this phenomenon has been explained by the filling of the d-states at the Fermi level of tungsten by the alloying carbon [12,13]. The promising electrocatalytic activity of the different materials has drawn considerable attention [14], since it resembles that of the precious metals without sharing their disadvantages like the liability to poisoning and deactivation. Therefore, one of the primary interests in the application of these carbides and nitrides is their application as cheap alternative catalysts to replace the group VIII noble metals, e.g. for hydrogenation [15] and especially in electrocatalysis [10,16]. Particularly tungsten carbide has been studied and proposed as a fuel cell anode catalyst that allows not only the oxidation of hydrogen but also of further, low molecular organic compounds like formate and methanol [17–25]. Tungsten carbide has also been suggested as cathode catalyst for the hydrogen evolution reaction in conventional (PEM) [26–29] as well as in microbial

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electrolysers [30]. Although related materials like molybdenum and tungsten sulfides [31,32] have also been proposed as hydrogen evolution electrocatalysts, so far no systematic or comparative study on further group IVB–VIB transition metal based compounds (carbides, nitrides, sulfides, etc.) has been published.

In this study we have investigated 18 different IVB–VIB transition metal carbides, nitrides, sulfides, silicides and borides, as well as three main group refractory ceramics, AlN, B₄C and h-BN on their suitability to act as hydrogen evolution electrocatalysts in acidic electrolyte solutions. All samples originate from industrial production and thus represent materials that can be used in realistic scenarios of large scale HER electrolyser application. Noteworthy, in contrast to highly specialised laboratory-based synthesis, present industrially feasible large scale fabrication does not allow the production of large surface area catalyst materials. As a consequence the materials used in this study possessed comparably low BET surface areas, causing an expectable low electrocatalytic performance. Nevertheless, the similar BET surface areas of the different catalyst compositions allowed a systematic comparison of the respective commercially available materials.

2. Materials and methods

2.1. Chemicals

All chemicals were obtained from Sigma–Aldrich, Germany and of analytical grade and used for electrode preparation or for electrolyte solution without further purification. Electrolyte solutions were prepared using de-ionised water and concentrated sulphuric acid. The concentration was adjusted to 0.1 mol L^{−1}. Nitrogen (99.99%) was received by Linde Gas, Germany, hydrogen (99.999%) was received from Westfalengas, Germany. Nickel powder (<10 μm, 99%) was received by Chempur (Karlsruhe, Germany), Pt–Vulcan (20 wt.% on Vulcan XC-72) by e-tek (Rodenbach, Germany) and Vulcan (XC-72R) by Cabot Corp. (Boston, USA).

2.2. Catalyst synthesis

All carbides, nitrides, sulfides, silicides and borides used in this study were commercial powders delivered by H.C. Starck GmbH (Germany). They were used for the electrode preparation as received, i.e. without further purification. All samples were derived from industrial synthesis routes and possessed an average purity of >98%. Main impurities were respective precursor components (the case syntheses based on metal oxides), iron and elemental carbon in the case of carbides. In the following a summary on the principle synthesis routes is provided:

Aluminium nitride (AlN) and titanium nitride (TiN) were produced by direct nitridation of metallic Al or Ti with N₂ at a temperature of >1000 °C. Hexagonal boron nitride (h-BN) was obtained from boric acid and melamine in nitrogen atmosphere at 900–1000 °C. Boron carbide (B₄C) was gained by carbothermal reduction of boron oxide (B₂O₃). Zirconium diboride (ZrB₂) was synthesised from zirconium oxide (ZrO₂) using a combined boro-/carbothermal reduction. Titanium diboride (TiB₂) and tungsten boride (WB) were gained from the respective oxides (TiO₂ and WO₃) using boro-/carbothermal reductions in vacuum. Molybdenum disilicide (MoSi₂) was obtained by igniting a mixture of molybdenum and silicon powders. Tungsten disilicide (WSi₂) was prepared from a mixture of tungsten and silicon powders in a vacuum furnace. Tungsten sulfide (WS₂) was gained by a direct reaction of tungsten with S₈ at 600 °C. Molybdenum carbide (Mo₂C), tungsten carbide (WC), niobium carbide (NbC), tantalum carbide (TaC), vanadium carbide (VC) as well as tungsten titanium carbide (WTiC) and tantalum niobium carbide (TaNbC) were gained

from direct carburisation of the metal powders. Titanium carbide (TiC) was obtained from direct exothermic reaction of well mixed Ti and C powders after initial ignition. Tantalum nitride (Ta₃N₅) was prepared by ammonolysis of tantalum oxide (Ta₂O₅) at 800 °C. Finally, titanium molybdenum carbonitride (TiMoCN) and tungsten titanium carbonitride (WTiCN) were gained from TiC, TiN, and carbon powder (and furthermore metallic Ti and Mo for TiMoCN) employing a high-frequency heating coil in N₂ atmosphere.

2.3. Electrode preparation

The electrodes used for this study were polycrystalline graphite rods (Elektrokohle Lichtenberg, Germany), paraffin impregnated, in order to prevent electrolyte solution to penetrate the graphite material [33]. The electrode diameter was 4.9 mm. Two different preparation techniques were employed to modify the electrodes with the electrocatalyst material

- (i) *Binder-based electrocatalyst immobilisation (paste electrodes)* [34]: The electrocatalyst was mixed manually with 10 μL of a 5 wt.% Nafion solution and about 5–10 mg (depending on the density of the electrocatalyst) of the mixture were transferred and hand-pressed onto the lower circular surface of the graphite rod and was allowed to dry at room temperature overnight.
- (ii) *Mechanical immobilisation (voltammetry of immobilised particles)* [33,35]: About 1 mg of the sample powder was placed on a glass plate. The electrode was gently rubbed over the material in order to immobilise compound at the electrode disc surface. Due to the softness of the polycrystalline graphite electrode and the hardness of the refractory powders a good adherence of particles at the electrode surface was assured. On average the amount of sample material adhering to the surface of the electrode (0.19 cm²) was between 50 and 100 μg. After the measurement, the electrode surface was cleaned by scraping off the upper electrode disc layer with a razor blade.

In this study the technique of mechanical immobilisation was used for two reasons: first of all, it allows a very rapid screening of different electrocatalysts in a short time. Thus, the electrode preparation and cleaning is a matter of seconds. Furthermore, only minute amounts (1 mg) of substance are required per measurement. Thus, screening processes are possible even with substances that are not available at larger quantities.

Certainly, the mechanical immobilisation is an only semi-quantitative method, since the amount of immobilised compound cannot be exactly controlled, however, as demonstrated in this manuscript (e.g., in Fig. 4) it is well suited for a material screening and comparative evaluation.

2.4. Electrochemical characterisation

100 mL of a 0.1 M H₂SO₄ served as the electrolyte solution. In all experiments, these solutions were purged with nitrogen for 10 min prior to the experiments in order to remove oxygen. All electrochemical experiments were carried out using a three electrode setup. A platinum wire served as the counter electrode and an Ag/AgCl (sat. KCl) electrode (Sensortechnik Meinsberg, Germany, 0.197 V vs. SHE) as the reference electrode. All experiments were performed using an Autolab PGSTAT 20 potentiostat/galvanostat (Ecochemie, Netherlands). In order to suppress mass transfer limitations all electrochemical experiments were performed using a rotating electrode setup [22,30,34]. For this purpose, the working electrodes were mounted at a rotating disc electrode device (RDE 616, EG&G, USA) and were rotated at a rate of 1000 rpm. Cyclic voltammetry (CV) was used at a scan rate of 5 mV s^{−1}.

Table 1

Overview of the catalyst materials studied in this work, and their BET surface area. Highlighted in grey are the benchmark materials.

Catalyst	BET [m ² /g]	Catalyst	BET [m ² /g]	Catalyst	BET [m ² /g]
1 Pt-Vulcan (20 wt.%)	170	9 NbC	1.80	17 VC	2.50
2 Ni powder	0.38	10 Ta ₃ N ₅	8.69	18 WB	0.20
3 Graphite powder		11 TaC	1.80	19 WC	4.72
4 AlN	2.00	12 TaNbC	8.84	20 WS ₂	3.72
5 B ₄ C	0.30	13 TiB ₂	3.25	21 WSi ₂	1.06
6 BN	5.90	14 TiC	3.00	22 WTiC (50/50)	2.33
7 Mo ₂ C	0.92	15 TiMoCN	1.84	23 WTiCN	1.93
8 MoSi ₂	1.35	16 TiN	3.60	24 ZrB ₂	1.62

For steady-state operation and corrosion tests chronoamperometry was performed as follows: the respective paste electrodes were immersed in a constant volume of 0.1 M H₂SO₄ and polarised at a constant potential of −1 V. After about 15–20 h the metal concentration in the electrolyte solution was analysed by ICP-OES.

All electrochemical characterisations were performed, at least, in triplicate. The standard deviation for the derived onset potential and overpotential data was usually below 35 mV.

The formal potential of the hydrogen evolution reaction was determined potentiometrically using a GPHR 1400A digital pH/mV-meter (Greisinger Mess- und Regeltechnik, Germany), a freshly platinised platinum wire as sensing electrode and an Ag/AgCl electrode as reference electrode.

2.5. Solution analysis

For the quantification of catalyst degradation/corrosion processes the concentration of the respective metal ions in the electrolyte solutions was analysed using ICP-OES (ICP-OES Vista MPX, Varian, Germany). The detection limit was generally <0.05 mg L^{−1}.

2.6. Surface characterisation

For all samples, the BET surface area was determined using a BET surface area and pore analyser (Gemini V, Micromeritics, USA) with nitrogen gas (99,999%) as adsorbate. The samples were heated to 200 °C for 2 h before being transferred to the analysis port. The relative pressure ranged from 0.05 to 0.3. All BET surface analyses were performed at least at two independent samples.

3. Results and discussion

Table 1 provides an overview of the different materials studied in this work, ranging from typical main group based covalent ceramics such as AlN, BN and B₄C to the group IVB–VIB transition metal carbides, nitrides, sulfides, silicides and borides.

Table 1 also shows that none of the tested compounds exhibits a large specific surface area that would be expected for a practical electrocatalyst application and that often was reported for lab-based, low-quantity syntheses. The reason for the low surface area is the industrial production process that at present does not allow the synthesis of large surface area compounds. Nevertheless the selection of compounds represents an ideal basis for the study of fundamental electrochemical properties, a systematic material comparison and a screening of “ready-for-use” materials.

The first three samples in Table 1, highlighted in grey, served as the reference materials. Here, Pt on carbon powder served as the upper benchmark electrocatalyst for hydrogen oxidation and evolution, and graphite powder as an “inert”, i.e., non-electrocatalytic, electrode substrate material. Furthermore, Ni, which is frequently used as a non-noble alternative for the electrochemical hydrogen evolution was used as a reference electrocatalyst.

Fig. 1 depicts exemplary cyclic voltammograms for the hydrogen evolution at selected carbides in comparison with platinum and graphite as reference materials. In this figure beside the reference electrode related potential scale (lower X-axis) an overpotential scale (upper X-axis) is drawn. The overpotential is one of the main criteria in the evaluation of the performance of electrocatalysts, as it allows their assessment in relation to the (thermodynamically determined) redox potential of the reaction for a given condition. In order to derive the respective overpotential data, the formal potential of the H₂/2H⁺ redox couple was measured using potentiometry. It was determined with $E_{\text{H}_2/\text{H}^+}^{\text{f}} = -230 \text{ mV}$ (vs. Ag/AgCl, sat. KCl).

Fig. 1 qualitatively illustrates the differences in the performance of selected electrocatalyst materials. Platinum is the electrocatalyst at which the hydrogen evolution proceeds with the lowest overpotential, followed by different carbides. The lowest performance, i.e. the highest overpotential, is observed for boron nitride. Its performance is even lower than that of the electrode support material (carbon).

In order to quantify the differences in the electrocatalyst performances the overpotential of the electrode reaction was determined by means of (i) measuring the overpotential at a fixed current density, and (ii) at the onset of the electrochemical reaction. The latter method—the determination of the so-called onset potential, E_{onset} , is an often used but nevertheless not a standardised or even clearly defined technique. By definition the onset potential describes the potential (or the overpotential) at which the electrochemical reaction commences [36]. For this study the onset potential of the

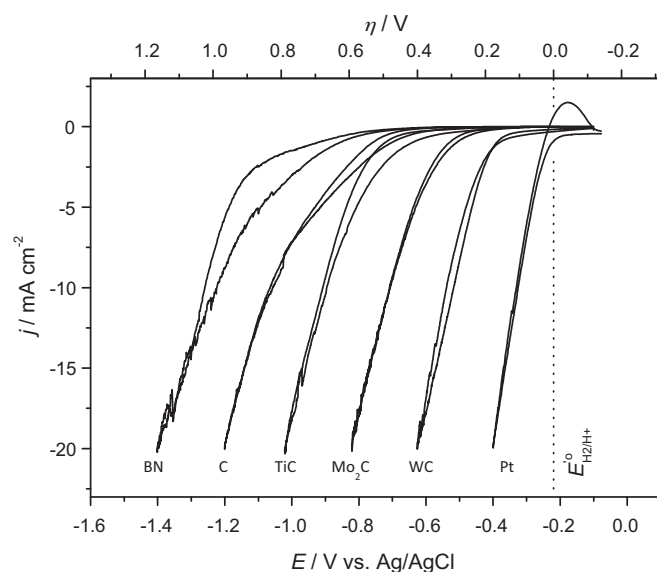


Fig. 1. Comparison of the electrocatalytic hydrogen evolution reaction of selected electrocatalysts by cyclic voltammetry. The catalyst samples were mechanically immobilised on a graphite electrode and immersed in 0.1 M H₂SO₄. The scan rate was 5 mV s^{−1}; the electrodes were rotating at 1000 rpm.

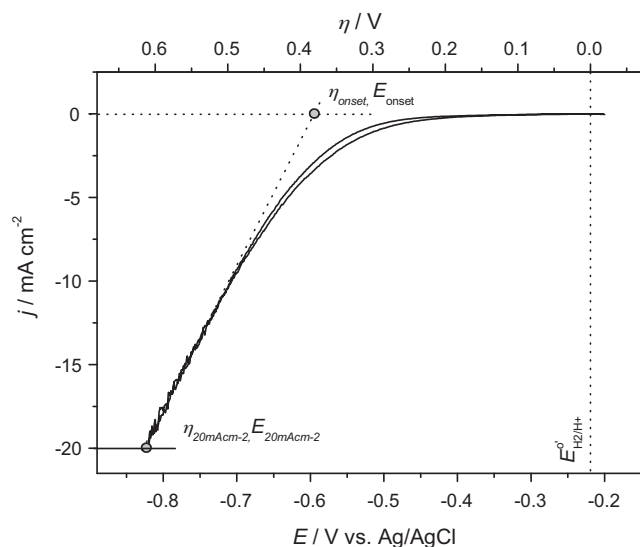


Fig. 2. Determination of the onset potential (E_{onset} , η_{onset}) of the hydrogen evolution reaction by means of a tangent method and the determination of ($E_{20 \text{ mA cm}^{-2}}$, $\eta_{20 \text{ mA cm}^{-2}}$). The example shows the electrocatalytic hydrogen evolution at microparticles of molybdenum carbide mechanically immobilised at a graphite electrode and immersed in 0.1 M H_2SO_4 . The scan rate was 5 mV s^{-1} ; the electrode was rotating at 1000 rpm.

hydrogen evolution reaction was defined as the intersection of the extrapolated baseline current and the prolonged tangent of the linear hydrogen evolution region of the catalytic curve (see Fig. 2). Due to its experimental robustness for the used catalyst materials and the ease of use this method was given preference over the Tafel analysis.

Additionally to the onset overpotential, η_{onset} , the overpotential at a fixed current density, here at 20 mA cm^{-2} , $\eta_{20 \text{ mA cm}^{-2}}$, was taken as a measure of the electrocatalytic activity. The latter current density refers to the projected surface area of the electrode. It is important to notice that in the case of mechanically immobilised particles the electrode surface is only partly covered with electrocatalytically active material [33,37,38]. Thus, the current density of the electrode is considerably lower than that of a fully covered electrode, like, a catalyst-Nafion paste modified electrode, used for comparison in this study. This is exemplarily illustrated in Fig. 3 for tungsten carbide modified electrodes. Here, the current density of the paste electrode is about 2.5 times higher than that of the mechanically modified, i.e. only partly covered, electrode. Whereas the current densities of both electrode types differ due to the differing amounts of electrocatalyst material, the onset-potentials are closely similar.

Table 2 and Fig. 4 provide a thorough analysis of the hydrogen evolution overpotentials at all tested electrode materials. Fig. 4 clearly demonstrates the strong correlation of the onset overpotentials and the overpotential data obtained at 20 mA cm^{-2} , verifying the experimental method and the data analysis.

Fig. 4 also shows that, as expected and generally accepted, platinum offers the lowest overpotential for the hydrogen evolution reaction among all catalysts investigated. It is followed by tungsten carbide and with a considerably increased overpotential by molybdenum carbide. At the opposite side, aluminium and hexagonal boron nitride modified electrodes show hydrogen evolution overpotentials higher than bare carbon. This result is not unexpected since these main group element based materials (which are referred to as covalent ceramics) lack the electrocatalytic-relevant d -electrons. They are further insulators with wide band gaps of 6.2 eV and 5.2 eV, respectively and conductivities of 10.8 S m^{-1} for AlN [39] and 10.12 S m^{-1} for BN [40]—which leads to an

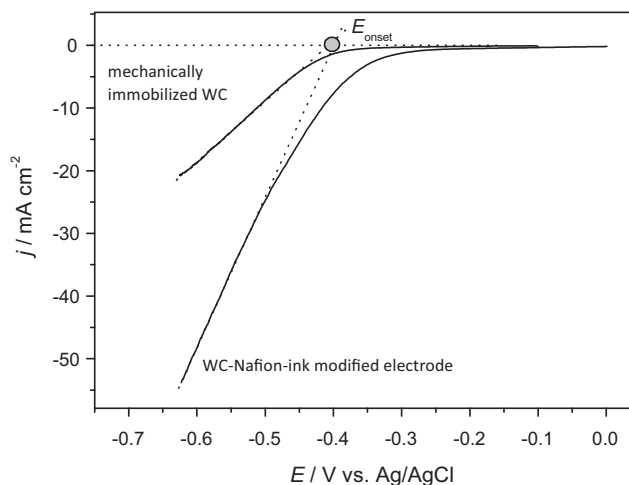


Fig. 3. Comparison of exemplary linear sweep voltammograms of a WC/Nafion ink-modified graphite electrode and a graphite electrode modified by mechanical immobilisation of WC microparticles. The electrodes were immersed in 0.1 M H_2SO_4 . The scan rate was 5 mV s^{-1} ; the electrodes were rotating at 1000 rpm. The current density refers to the total geometric electrode surface area.

electrochemical isolation of the electrode surface upon immobilisation of these compounds.

The majority of the studied transition metal compounds possess overpotentials that lie in the midfield between platinum and carbon. In order to elucidate correlations between catalyst composition and performance a three-dimensional plot of the overpotential data as a function of the metal and the non-metal composition of the respective compounds is presented in Fig. 5. This figure shows that tungsten represents the preferred metal component. In comparison to the other transition metals the tungsten-based materials possess the highest electrocatalytic activity. This is most obvious for the carbides (for which also the highest number of different compounds was available for this study). Tungsten is followed by molybdenum, which may still represent the basis for promising catalysts. The compounds of all other metals (Nb, Ta, V, Ti and bimetallic systems based on WTi or TaNb combinations) do not appear to possess sufficient electrocatalytic activity for the HER to justify further in-depth research. As discussed earlier, the least active metals are zirconium and, due

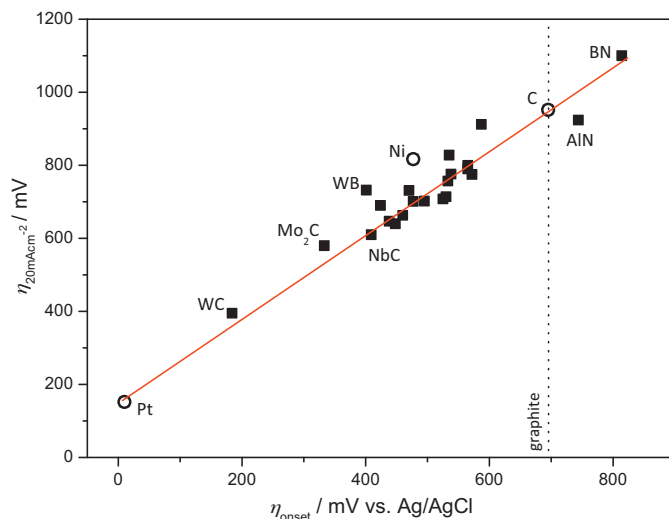


Fig. 4. Correlation of the overpotential of the hydrogen evolution reaction at a current density of 20 mA cm^{-2} and the onset overpotential. The catalyst samples were mechanically immobilised at a graphite electrode and immersed in 0.1 M H_2SO_4 . The scan rate was 5 mV s^{-1} ; the electrodes were rotating at 1000 rpm.

Table 2

Detailed analysis of the overpotential data and corrosion rates of the electrocatalysts studied in this work. The overpotential data are based on electrodes with mechanically immobilised catalyst particles, the corrosion data were obtained using catalyst/Nafion paste modified electrodes.

Catalyst sample	E_{onset} [mV] (vs. Ag/AgCl)	η_{onset} [mV]	$\eta_{20\text{ mA cm}^{-2}}$ [mV]	k_{corr} [$\mu\text{mol d}^{-1}\text{ cm}^{-2}$]
1 Pt-Vulcan (20 wt.%)	–240	10	201	0.36
2 Ni-powder	–707	477	866	–
3 Graphite powder	–925	695	1001	–
4 AlN	–974	744	973	17.04
5 B ₄ C	–817	587	961	13.94
6 h-BN	–1044	814	1149	3.072
7 Mo ₂ C	–563	333	629	152.81
8 MoSi ₂	–755	525	757	8.21
9 NbC	–639	409	659	0.62
10 Ta ₃ N ₅	–760	530	763	1.30
11 TaC	–654	424	739	0.36
12 TaNbC	–765	535	877	0.12
13 TiB ₂	–763	533	806	31.99
14 TiC	–802	572	824	1.56
15 TiMoCN	–795	565	849	12.38
16 TiN	–768	538	825	51.36
17 VC	–678	448	689	24.02
18 WB	–631	401	781	22.97
19 WC	–414	184	444	5.64
20 WS ₂	–707	477	750	0.43
21 WSi ₂	–690	460	712	1.01
22 WTiC	–668	438	696	1.20
23 WTiCN	–725	495	751	6.91
24 ZrB ₂	–795	565	839	56.66

to the lack of *d*-electrons, the main group metals aluminium and boron.

On the non-metal side, the carbides represent the most promising group of refractory compounds. They are followed by borides, silicides and sulfides, with the respective nitrides being the least active materials.

For technical HER-electrolysis, the durability, i.e. life time, of any catalyst is an additional important feature which has a major impact on the catalyst applicability [22,41,42]. For this reason we also studied the stability of all electrocatalysts under hydrogen evolution (constant polarisation) conditions. As Table 2 illustrates the resulting corrosion rates, k_{corr} , provide a rather scattered picture. Corrosion rates between 0.1 and 152 $\mu\text{mol}_{\text{catalyst}}\text{ d}^{-1}\text{ cm}^{-2}$ were measured. The latter value – the by far lowest stability for the materials under investigation – was determined for molybdenum carbide, Mo₂C. In contrast to its good electrochemical performance

(and despite of its low BET, see Table 1) this material possesses the highest dissolution rate. With 5 $\mu\text{mol}_{\text{catalyst}}\text{ d}^{-1}\text{ cm}^{-2}$ the corrosion rate of WC is acceptable. Yet, it is two orders of magnitude higher than that of lab-made WC samples reported in a previous study of our group [30]. This leads us to the conclusion that not only the electrocatalytic activity but also the stability of these materials strongly depend on the respective catalyst synthesis.

4. Conclusion

We have systematically studied and compared a wide set of transition metal carbides, nitrides, sulfides, silicides and borides – all derived from industrial preparation routes – as catalysts for the electrochemical hydrogen evolution reaction. We employed the voltammetry of immobilised microparticles as an excellent tool for a rapid electrocatalyst screening and characterisation as well as studies on paste electrodes. By assessing the materials' activities and stabilities we demonstrate that a variety of different transition metal-based ceramics is available as promising low cost hydrogen evolution electrocatalysts. Especially the electrocatalytic properties of compounds like tungsten and molybdenum carbide but also of tungsten boride calls for continuative research and development, as hydrogen production by electrolysis will certainly be seminal technology. Here one may also consider the use of these materials as substrates to support low coverages of Pt, as reported previously for the example of tungsten carbide [43,44].

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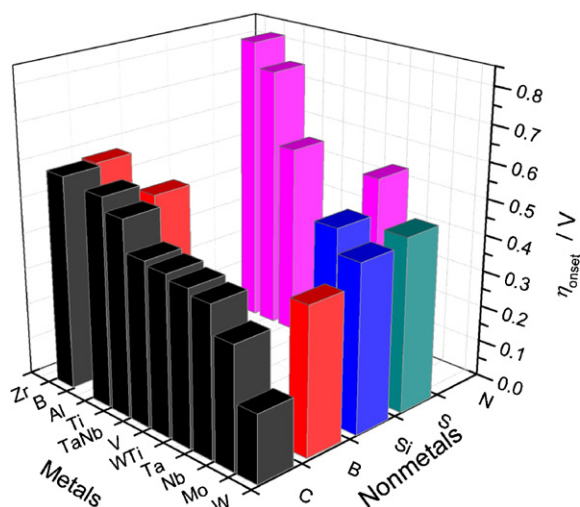


Fig. 5. 3-dimensional plot of the onset overpotential for the hydrogen evolution reaction at the studied refractory ceramics as a function of their metal and non-metal components. The data are based on electrodes prepared via mechanical catalyst immobilisation. Low columns represent a high performance; high columns represent low catalytic activity.

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